OXIDE FILMS ON GOLD ELECTRODES

L. Kékedy and A. Popescu

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16. Abstract

The literature on the formation of oxide films on gold electrodes under various conditions is reviewed. Experimental data are presented as well as data on the nature of these films, methods of pretreatment and applications. The literature survey ends in the summer of 1972 (supplemented until the fall of 1973 after the paper was submitted).

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OXIDE FILMS ON GOLD ELECTRODES

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1. General Information

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A main objective of instrumental analytical chemistry is experimentation with transducers for certain determinations. Transducers are devices for the transformation of a characteristic parameter of the system into a parameter of a different nature, e.g., of concentration into an electric signal. We call such transducers "electrodes." The main feature of a transducer, i.e., of an electrode, from both theoretical and practical viewpoints, is the transfer function: the ratio of the magnitude of the input signal (concentration) to the magnitude of the output signal (current, potential).

An essential condition of this function is its constancy, i.e., it should not vary depending on the experimental conditions. With regard to an electrode, this means that it should be inert, i.e., that is should be either a source or an acceptor of electrons and should not participate in any other way in the changes taking place in the system.

Gold occupies the first place in the scale of the thermodynamic nobility of metals and the fourth place, after Rh, Nb and Ta, in the scale of practical nobility [1], and it is far from being as noble and indifferent as it was thought for a long time to be. Its electrochemical behavior places it among the normal metals and among the inert metals [2]. Numerous studies

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* Numbers in the margin indicate pagination in the foreign text.

performed with electrodes made of noble metals have shown that the reproducibility and the shape of the titration curves, and of the i - E curves are largely dependent on the state of the electrode surface.

2. Oxidized Surfaces

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Following anodic polarization, the gold becomes covered with a film of adsorbed oxygen and oxide equivalent to 600-1000 $\mu C/cm^2$. The presence of oxides at the surface of the gold is explained by several authors [3-13], who studied the anodic oxidation of gold in acid, neutral or alkaline solutions at a low density of the current. At first Au_2O is formed, followed by AuO and by Au_2O_3 prior to the liberation of oxygen.

Using the oscillographic method, Hickling [14] noted that the only stable oxide is Au_2O_3 in the form of a unimolecular film. Analyzing the polarization curves obtained by El Wakkad and A.M. Shams [15] in various media, one can see that the starting potentials of the three steps on the curves of anodic polarization correspond to the equilibrium potentials of the systems Au/Au_2O, Au/AuO and Au/Au_2O_3 (Table 1). This proves that Au_2O, AuO and Au_2O_3 are formed at the gold surface prior to the liberation of oxygen. The starting potentials are not in agreement with the redox potentials of higher and lower oxides, but rather with the potentials corresponding to the Me/MeO system; this points to the instability of lower oxides in aqueous solutions, as confirmed by the observations of other authors [4-7].

From measurements of the capacity of the double layer, it results that the thickness of these oxide films corresponds to two molecules. The different behavior of gold in alkaline solutions is said by Armstrong [12] to be the cause of the amphoteric /687
nature of gold oxide which forms aurites and aurates in alkaline solutions.

Grüneberg [16] followed the behavior of gold electrodes, by means of the charging curves in sulfuric acid, in a potential range starting at -650 mV (liberation of hydrogen) and up to 2200 mV (liberation of oxygen). Prior to oxidation, the electrodes were treated in the following manner:

a) immersion in royal water, washing with bidistilled water and cathodization in dilute potassium hydroxide;

b) anodization of the electrode in concentrated potassium hydroxide or in sulfuric acid so that no visible signs appear on the surface of the electrode;

c) strong anodization so that a largely visible layer appears on the surface of the electrode.

These layers appear blue when thin (<1000 Å) and greenish when thicker than 100 Å. Cathodic reduction causes a change in the color of the layer to black. No unified concept exists on the stoichiometric composition of the oxide layers and on the reversible potentials of these oxides.

Milazzo [17] assumes that the following reactions takes place:

$$2\,Au(s) + 3H_2O \rightarrow Au_2O_3(s) + 6H^+ + 3e^- \quad 1.363\ V \qquad (1)$$

$$Au(s) + 3H_2O \rightarrow Au(OH)_3 + 3H^+ + 3e^- \quad 1.450\ V \qquad (2)$$

Other authors [18-19] found a value of 1.363 V for the reversible potential in reaction (2). Barnartt [20] analyzed the oxide deposit obtained after 23 hours at a current density of 10 mA/cm^2 and found $Au(OH)_3$ as the hydrolysis product of Au_2O_3, in agreement with the studies of Vetter and Berndt [21]. The following reaction is commonly assumed to take place in acid solutions for the formation of hydroxides:

TABLE 1. STARTING AND EQUILIBRIUM POTENTIALS OF GOLD IN VARIOUS MEDIA

Solution	E_{start}			$E_{eq.}$		
	I tr.*	II tr.	III tr.	$Au-Au_2O$	$Au-AuO$	$Au-Au_2O_3$
0.1N H_2SO_4	+0.27	+0.96	+1.26	+0.36	+0.98	+1.30
Phosphate buffer	−0.05	+0.62	+0.86	0.00	+0.62	+0.91
0.1M Na_2CO_3	−0.25	+0.16	+0.70	−0.24	+0.38	+0.79

* Steps on the curve of anodic polarization

$$Me + H_2O \rightarrow Me-OH + H^+ + e^- \quad (3)$$

Two slow reactions are possible for the formation of oxides:

$$Me + H_2O \rightarrow Me-O + 2H^+ + 2e^- \quad (4)$$

$$Me-OH \rightarrow Me-O + H^+ + e^- \quad (5)$$

In addition, there is the possibility of a reduction of the type:

$$2Me-O + 2H^+ + 2e^- \rightarrow 2\,Me + H_2O_2 \quad (6)$$

The concentrated sulfuric acid activates the following reactions: %688

$$Au(OH)_2 \rightarrow AuO(OH) + H_2O \quad (7)$$

$$2Au(OH)_2 \rightarrow Au_2O + H_2O \quad (8)$$

$$2Au(OH)_3 \rightarrow Au_2O_3 + 3H_2O \quad (9)$$

The characteristic "differential capacity vs. potential" curves (Fig. 1) show that concentrated sulfuric acid has the effect of lowering the amount of hydroxides, while the amount of oxyhydrates and of oxides increases. There was an increase in the amount of oxides appearing in the anodic cycle in the potential range of +1400 mV to +1800 mV.

Shutt and Walton [9] showed that a mono- or bimolecular layer of Au_2O_4 is formed in sulfate solutions, which breaks down to $Au_2O_3 + 1/2\ O_2$ after cessation of the anodic current.

Studies on the resting potential showed that gold can adsorb a monolayer of oxygen atoms at a potential of +0.9 V [13-22].

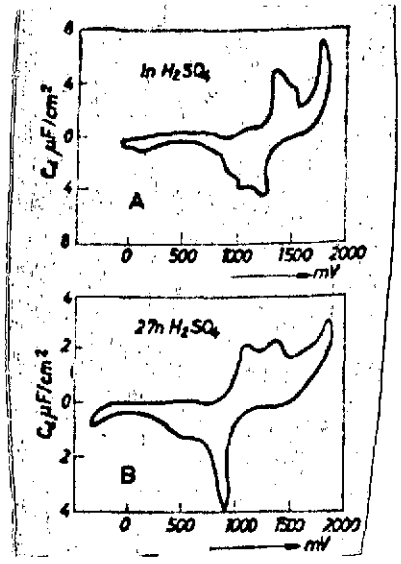

Fig. 1. Differential capacity as a function of potential for gold electrodes placed in H_2SO_4. A. 1 N H_2SO_4; B. 27 N H_2SO_4.

Similar conclusions were drawn from measurements of the capacity of the double layer [23]. Such a system, which was not preliminarily analyzed, is the Au/AuO electrode. A red-brown hydrated film of Au_2O_3 appears on the gold surface if the adsorbed layer of oxygen is formed by anodic polarization above 1.360 V [20]. This system forms an Au/Au_2O_3 electrode. It is assumed that the Au/Au-O electrode is a polyelectrode [24], its resting potential being a mixed potential [25], while the Au/Au_2O_3 electrode is a simple electrode, its resting potential being an equilibrium potential.

Several authors [26] followed the state of the oxygen adsorbed on gold electrodes and made potentiostatic measurements at a potential varying between 1.35 and 1.60 V in 2 N sulfuric acid saturated with argon at 25°C. The adsorption time was changed from 10^{-3} sec to several scores of seconds. The oxygen adsorbed on the gold appeared in two forms: a less stable form which was reduced at 1.30-1.35 V and a more stable form which was reduced at a more negative potential (by 0.4 V).

Studies on the over-voltage of oxygen on shining gold [27] /689
provided information on the kinetics of oxygen reduction at this electrode. Using electrodes of the type Au/Au-O and Au/Au_2O_3 in 2 N solutions of sulfuric acid saturated with oxygen, it was concluded that the rate-limiting step in the reduction of oxygen at the Au/Au-O electrode is:

$$O_2(ads.) + e^- \rightleftharpoons O_2^- \text{ (ads.), cu } i_0 = 1.3 \cdot 10^{-11} \text{ A/cm}^2.$$

Oxygen liberation could not be studied on this type of electrode, because the anodic process transforms the Au/Au-O electrode into an Au/Au_2O_3 electrode. This is a simple electrode with E_0 = 1.360 V [14], a value obtained by extrapolating the curves of anodic and cathodic polarization of the Au/Au_2O_3 couple. The processes taking place at this electrode are the formation and reduction of the oxide Au_2O_3.

Barnartt [20] showed that the Au_2O_3 film is weakly attached to the surface of the electrode and is readily exfoliated. In such a manner, new areas of gold become available for the continued formation of Au_2O_3.

The presence [23] or absence [15, 31] of intermediary products at the gold surface on the pathway of formation of the Au (III) oxide could be demonstrated by studying the state of the gold surface using known techniques, such as chronopotentiometry [12, 28], voltametry [29], triangular cyclic voltametry [30] or chemical methods [12, 31] in perchloric acid.

Laitenen and Chao [33] followed the behavior of gold and perchloric acid at a constant current of anodization or cathodization; the results are presented in Fig. 2. There is a marked increase in potential in the anodization stage (O_a) as compared to the cathodization stage (O_c). Following a strong anodization, there is a rapid increase in the amount of oxide per unit area (Q/A) at potential values higher than 1.95 V, indicating that the gold surface was oxidized in depth (Fig. 3). The oxides formed at these potentials were colored black to orange and could be separated. The composition of these layers revealed a thick layer of Au_2O_3 [5].

Two types of hysteresis curves were recorded while following the change in the same ratio Q/A as a function of the anodization potential (Fig. 4): the dotted lines represent the same

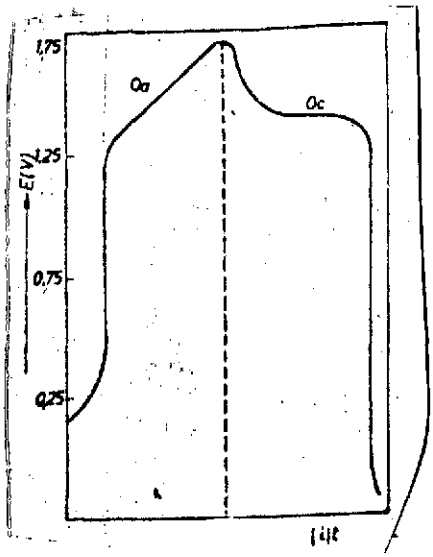

Fig. 2. Anodic-cathodic chronopotentiogram of gold in H_2SO_4.

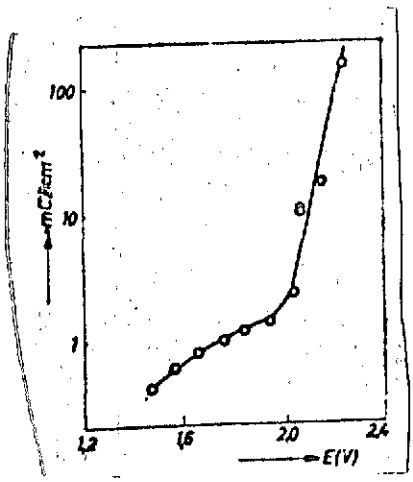

Fig. 3. Amount of oxide formed on gold (expressed in coulombs required for the reduction per unit area Q/A) as a function of the potential.

variation under conditions where the electrode was pre-anodized at higher potentials, while the solid line was obtained at lower pre-anodization potentials (0.65 V). These curves are evidence in favor of the following:

a) the superficial oxidation reaction is reversible;

b) the extent of the oxidation is not determined solely by the potential,

c) there appears to be only a stable form of oxide.

The properties of the anodic oxide films formed on gold electrodes were studied as a function of various parameters. Changes in the resting potential /690 were recorded for various time periods, at the end of which the Q/A ratios were determined. It was concluded that these ratios decrease in the course of time (Fig. 5), regardless of the utilized anodization potential, which shows that the extent of oxidation is not determined by the potential in particular.

2.1. Effect of Anodization Time

The curves illustrating the change in the Q/A ratio as a function of the time of anodization (Fig. 6) indicate that two reactions are taking place: an initial rapid /691

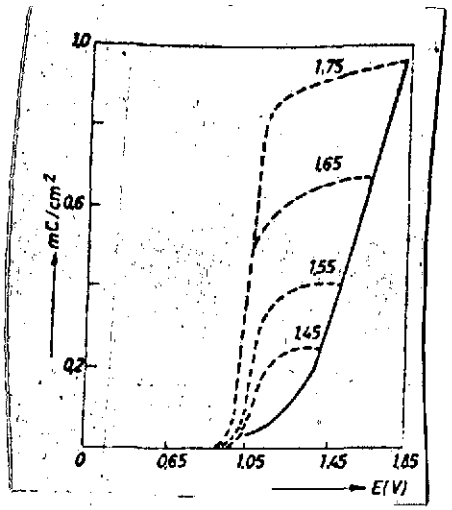

Fig. 4. Amount of oxide on gold as a function of potential and pretreatment. The figures on the dotted curves represent the potentials of pre-anodization. In the case of the solid curve, the pre-anodization is $\leq$ 0.65 V.

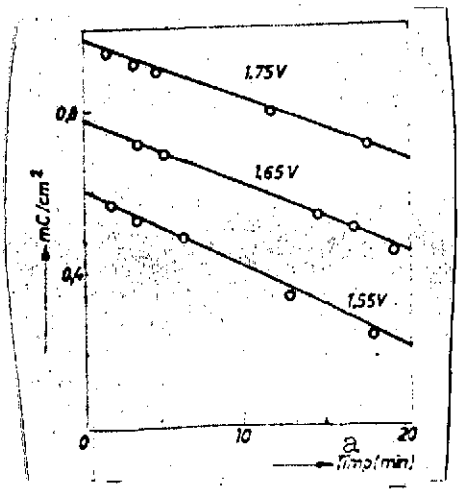

Fig. 5. Changes in the Q/A ratio as a function of time at various anodization potentials.

Key: a. Time

reaction followed by a slow reaction. The slow reaction represents the penetration of oxygen into the first atomic layers of the solid. The nature of these two reactions can be explained better by following the changes in the anodic current as a function of the time of anodization (Fig. 7). Each curve can be regarded as being composed of two parts: a rapid fall in the basic current and a small residual current. If the basic current can be identified with Q/A at a short anodization time, i.e., with the initial superficial oxidation, the residual current can be explained by a marginal diffusion of the oxygen atoms, like in the case of the platinum electrodes [34].

This phenomenon was observed upon microscopic examination of the electrode surface, which shows a stronger reaction with the marginal surface. Kinetic studies showed that this diffusion is related to the residual current. The appearance of a large residual current at higher potentials is due to the liberation of oxygen. A study of the change in the capacity of the double layer as a function of potential yields a curve with an inflexion point. The change in the capacity of the double layer at higher potentials shows that the superficial oxidation of the electrode starts at a potential of 1.25 V.

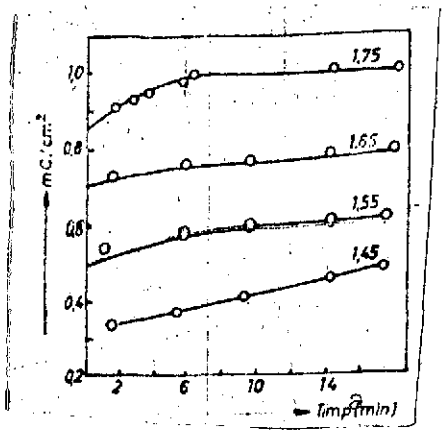

Fig. 6. Amount of oxide formed as a function of time and of the potential.

Key: a. Time

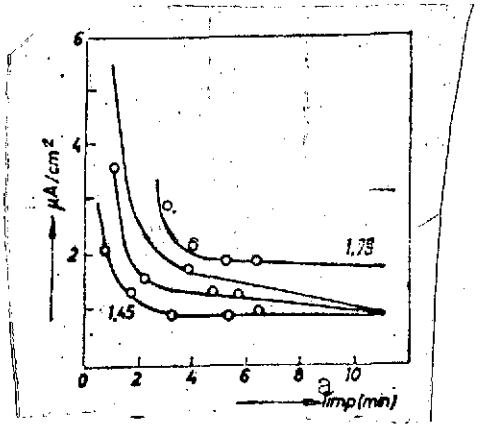

Fig. 7. Change in the anodic current as a function of time.

Key: a. Time

2.2. Effect of Current Density

A study of the change in the Q/A ratio as a function of current density showed an increase in this ratio with increasing current density. The anodic chronopotentiograms show no significant change in slope at a potential lower than 1.35 V and thus no sign of deposition. These observations are contrary to the conclusion of several authors [15, 31], who postulated the intermediate formation of Au_2O and AuO in the layers reported by them and tend to confirm the opinions according to which these are the effects of impurities [21, 28].

2.3. Effect of pH and Anions

Bode, Andersen and Eyring [35] studied these effects on the potential of zero charge (p.z.e.) of the gold electrode using a special technique which makes it possible to continually renew that surface /692 of the electrode which is in contact with the aqueous solution. This was done by rapid and repeated grating of the entire surface of the electrode in order to produce conditions of zero charge. A study of the change of this potential as a function of pH showed a deviation from linearity in the acid range only. The authors explain this deviation as being due to the adsorption of various anions and the appearance of a Faraday reaction at the electrode. The sequence of anion adsorption determined by the authors was the following:

$$I^- > Br^- > OH^- > Cl^- > ClO_4^- > SO_4^{2-} > F^-$$

Other authors [36] found that the anodic process on gold in chlorides and sulfates is controlled by diffusion, i.e., by the diffusion of anions as acceptors. Kinetic studies of these mechanisms led the authors to the finding of simultaneous formation and dissolution of the anodic layer in pure sulfate.

MacArthur [37] followed the electrochemical behavior of gold in alkaline cyanides and in citrate and phosphate buffers using cyclic voltametry and other galvanostatic techniques and he postulated the following two as possible reactions:

$$Au + CN^- \rightleftharpoons Au(CN)_{ads} + e^-$$
$$Au(CN)_{ads} + CN^- \rightleftharpoons Au(CN)_2^-$$

No oxidized species were obtained in buffer solutions.

2.4. Effect of Cations

Using the technique of cyclic voltametry, Lorenz, Maumitzis and Schmidt [38] demonstrated the adsorption of Ag^+ Tl^+ and Cu^{2+} on polycrystalline gold electrodes. It was found that the adsorption of these metals affects considerably the kinetics of the electrode reactions. Similar conclusions were reached when these effects were followed in aqueous solutions containing tetraalkylammonium and other cations [35]. It was concluded that the adsorption of cations takes place to a much lesser extent than the adsorption of anions; this preferential adsorption is enhanced by the presence of large cations. The orientation of ion pairs is related to the tendency of the metal to form coordination complexes with these ion pairs. The formation of the bonds Me-anion-cation explains the inhibition of corrosion by organic ions and also the different reaction rates [39].

2.5. Aging of Oxide Films

Brummer [40] studied the properties of anodic oxide films formed on gold electrodes in perchloric acid as a function of time and of the potential of formation, and found the following:

a) the oxide films increase in time according to a relationship of the type:

$$Q = a + b \log \tau,$$

where Q is the amount of oxide, a and b are constants and τ is the time of formation;

b) the rate of increase in the amount of oxide increases with the increase in the potential of formation; /693

c) the oxides formed during a longer time at a given potential are harder to reduce due to the fact that "aging" stabilizes the oxide, while the transport through this film of oxide is hindered.

d) the "aging" effect is stronger at low formation potentials although the thickness of the oxide formed at high potentials is larger;

e) due to this effect, the method of scanning the potential according to Will and Knorr [30] does not give satisfactory results when applied to this type of films.

It has been concluded from the performed studies that the mechanism of the anodic process involves the OH^- radical, like in the case of platinum [14, 41]:

$$Au + H_2O \rightleftharpoons Au....OH + H^+ + e^- \qquad (1)$$

The OH resulting from chemosorption leads to the reaction

$$Au....OH + \rightarrow AuO + H^+ + e^- \qquad (2a)$$

where AuO represents the layer of oxygen atoms resulting from chemosorption, or

$$\begin{aligned} Au....OH + H_2O &\rightarrow Au....OOH + 2H^+ + 2e^- \\ Au....OOH &\rightarrow Au + O_2 + H^+ + e^- \end{aligned} \qquad (2b)$$

The clean regenerated surface in (2b) may be used again (1). Subsequently, the oxidation may take place on the AuO surface.

$$AuO + H_2O \rightarrow AuO....OH + H^+ + e^- \qquad (3)$$

AuO...OH has the same empirical formula as the hydrated Au_2O_3 [42].

That the final product is Au_2O_3 was demonstrated by the value of 1.36 V for both the potential of the cathodic deposit and the potential of the electrode after opening of the circuit; this is the experimental value for the standard potential of $Au(OH)_3/Au$ [18, 43].

2.6. Resting Potentials in Various Oxidizing Media

The studies of Brummer and Makrides [44] showed that the resting potential is a function of the potential of formation of the oxide film and a function of pH; the resting potential falls off sharply with the decomposition of the oxide film on the surface of the electrode.

2.7. Pretreatments Used in Studies on the Resting Potentials /694

Üneri and Kabasakaloglu [45] followed the change in the potential of the gold electrode, reduced and oxidized in various media, as a function of time. A series of curves was obtained with distinct steps corresponding to the normal potential values given in the literature for the states of oxidation of gold. The steps of potential correspond to the equilibrium potentials of the metal oxides (Table 2).

The same authors [48] found that this type of curve changes in relation to the pretreatment of the electrode; the following pretreatment is recommended in order to obtain reproducible curves:

a) the gold electrode is introduced as the cathode into a 1 N sulfuric acid solution for 5 min at a current of 10 mA. Subsequently, it is introduced into a 1 N solution of sulfuric acid through which is passed a continuous current of nitrogen. The electrode potential is stabilized at 0.3 V, while the current falls to 0 μA.

According to the observations of Will and Knorr [49], the adsorption of oxygen on gold in sulfuric acid cannot take place at potentials lower than +0.85 V, while the adsorption of H_2 takes place below + 0.15 V. These types of electrodes, which are reduced at 0.3 V, are called "reduced electrodes."

b) the electrodes reduced by the above procedure is oxidized anodically for 5 min at 10 mA. These types of electrodes were called "oxidized electrodes."

Following such a pretreatment, the electrodes were used for determining the resting potential of gold in various media

TABLE 2. POTENTIAL VALUES OF GOLD-OXIDES SYSTEMS

Tabela 2

Potențialele sistemelor aur-oxizi

	Reactions	Potential (V)	
LATIMER [46]	1. $Au(OH)_3 + 3H^+ = Au + 3H_2O$	$E^0 = 1{,}45$	
	2. $2Au + 3H_2O = Au_2O_3 + 6H^+ + 6e^-$	$E^0 = 1{,}457 - 0{,}0591$ pH	
POURBAIX [1]	3. $Au_2O_3 + H_2O = 2AuO_2 + 2H^+ + 2e^-$	$E^0 = 2{,}630 - 0{,}0591$ pH	
	4. $Au + 3H_2O = H_3AuO_3 + 3H^+ + 3e^-$	$E^0 = 1{,}565 - 0{,}0591$ pH + 0,197 log (H_3AuO_3)	
	5. $H_3AuO_3 + AuO_2 + H_2O + H^+ + e^-$	$E^0 = 2{,}305 - 0{,}0591$ pH − 0,0591 log (H_3AuO_3)	
	6. $H_2AuO_3^- = AuO_2 + H_2O + e^-$	$E^0 = 1{,}611 - 0{,}0591$ log ($H_3AuO_3^-$)	
HOARE [47]	7. $Au\,O + 2H^+ + 2e^- = Au + H_2O$	$E^0 = 0{,}980 \mp 0{,}029$	
	8. $Au_2O_3 + 6H^+ + 6e^- = 2Au + 3H_2O$	$E^0 = 1{,}350 \mp 0{,}010$	
		0,1 N H_2SO_4	0,1 N Na_2CO_3
EL WAKKAD & SHAMS [15]	9. Au/Au_2O	0,36	−0,24
	10. $Au/Au - O$	0,98	0,38
	11. Au/Au_2O_3	1,30	0,70
		1 NH_2SO_4	0,1 N Na_2CO_3
LEE, ADAMS & BRICKER [11]	12. Au_2O/Au	0,42	0,24
	13. AuO/Au	1,04	0,38
	14. Au_2O_3/Au	1,36	0,70

TABLE 3. RESTING POTENTIALS AND STEPS OF POTENTIAL ON THE POTENTIAL-TIME CURVES WITH GOLD ELECTRODES OXIDIZED AND REDUCED IN VARIOUS MEDIA

Medium	Gold		Average resting potentials (V)
	Ox. (V)	Red. (V)	
10^{-2} M $Ce(IV)SO_4$ + 1 N H_2SO_4	1.262 ∓ 0.002 1.528 ∓ 0.008	1.557 ∓ 0.015	1.546
10^{-2} M $KMnO_4$ + 1 N H_2SO_4	1.393 ∓ 0.028 1.535 ∓ 0.008	1.522 ∓ 0.003	1.496
0.125 M $K_2Cr_2O_7$ + 1 N H_2SO_4	1.600 ∓ 0.010 1.273 ∓ 0.025	1.242 ∓ 0.013	1.256
0.125 M $K_2Cr_2O_7$ + 1 N HNO_3	1.305 ∓ 0.005	1.290 ∓ 0.000	1.251
0.250 M CrO_3	1.500 ∓ 0.002 1.265 ∓ 0.001	1.24	1.204
1 N HNO_3	1.575 ∓ 0.018 1.235 ∓ 0.019 1.265 ∓ 0.000 0.990 ∓ 0.001	1.081 ∓ 0.002	1.028
1 N H_2SO_4	1.585 ∓ 0.015 1.224 ∓ 0.008 1.270 ∓ 0.009 0.580 ∓ 0.018	0.543 ∓ 0.002	0.754
1 N H_2SO_4 + 10^{-2} M H_2O_2	1.060 ∓ 0.008 0.813 ∓ 0.022	0.855 ∓ 0.007 0.825 ∓ 0.005	0.826
1 N NaOH	0.407 ∓ 0.004	0.120 ∓ 0.017	0.207

(Table 3). It is seen that the resting potential is similar to the equilibrium potential of gold in the oxidized form.

That the potential does not remain constant at a certain value indicates the instability of the various forms of oxides in aqueous solution. The steps on the curves of the potential obtained with the gold electrode oxidized and reduced in 1 N sodium hydroxide, when compared to the equilibrium potentials in alkaline media, show that the electrodes can be oxidized in both alkaline and acid media.

3. Reduction of the Oxide Film

The reduction process was followed galvanostatically at different current densities between 10 and 1000 μA/cm^2 in a solution of perchloric acid for anodically polarized electrodes, between 1.2 and 1.85 V (related to E.N.H.) [44]. The measurements were not extended beyond 1.85 V in order to prevent extensive oxidation of the electrode surface [34]. The obtained cathodic chronopotentiogram shows, unlike the cathodic one, a clear and well-defined decrease of the potential, corresponding to the process of reduction of the superficial oxide layer. The change in cathodic charge as a function of the reduction time is a zero- /696
order reaction, suggesting solubilization processes, although the oxide disappears from the solution by a nonelectrochemical way. The rate of solubilization determined by this procedure is in good agreement with the results of others [33, 27]. The change of the cathodic charge with the formation potential leads the authors to conclude that at 1.45 V it is close to that of a simple layer (450 μC/cm^2), a result formerly found by Hickling [14].

A problem which has been under investigation for a long time is whether hydrogen peroxide exists as an intermediary in the electrochemical reduction of oxide films. An answer to this question has been sought by analyzing the galvanostatic curves of charging and discharging. Different authors obtained different results. Several authors [50-52, 14] found the anodic charge Q_a to be equal to the cathodic charge Q_k. Other authors [53, 54, 12, 21] found $Q_a = Q_k/0.5$. The latter result indicates that the decrease in the oxide layer takes place according to the /697
reaction

$$2Me{-}O + 2H^+ + 2e^- \rightarrow 2Me + H_2O_2$$

and stops at the hydrogen peroxide step.

The experimental results show that the hydrogen peroxide formed as a result of cathodic polarization of gold in 1 N H_2SO_4 in the range where the oxide film is reduced (+1350 mV to +850 mV) is not reduced electrochemically. The reduction takes place below 600 mV.

Shutt and Walton [9] found that the oxide layer produced in the Au/1 N H_2SO_4 system in the potential range 1370–1750 mV is reduced by a pathway which does not involve hydrogen peroxide. It remains to be seen if this holds true also for the oxyhydrates and the oxides produced at higher potentials.

3.1. Kinetics of Reduction of the Oxide Films

Assuming that Au_2O_3 is the most stable oxide (at various hydration forms), Brummer and Makrides [44] studied the kinetics of reduction of the oxide films formed at various potentials as a function of pH, and found that the reduction of the oxide film is related to the potential of formation of the oxide and not to the thickness of the oxide film. In order to estimate the exchange current, it was assumed that the reversible potential is determined by the reaction:

$$Au(OH)_3 + 3H^+ + 3e^- \rightleftharpoons Au + 3H_2O$$

and is equal to 1.36 V [15, 18, 19]. The reduction current decreases logarithmically with the increase in the formation potential while the pH dependence of the latter is not significant.

$$(d \log i/d\ pH)_E = 1{,}39 \pm 0{,}02.$$

These authors found that the bulk of the oxide was reduced at a constant value of the potential; the process was hindered if the

oxide was formed at a higher potential. Taking into account these observations and the fact that the value of the Tafel slope (40 mV) implies a reduction with the participation of three electrons, the following mechanism was postulated for the reduction of oxide films on gold:

$$AuOOH + H^+ + e^- \overset{\text{rapid}}{\rightleftharpoons} AuO + H_2O \quad \text{(I)}$$

$$AuO + H^+ + e^- \overset{\text{slow}}{\longrightarrow} AuOH \quad \text{(II)}$$

$$AuOH + H^+ + e^- \overset{\text{rapid}}{\longrightarrow} Au + H_2O \quad \text{(III)}$$

where AuO is written as a state of oxidation of Au (II), while AuOH is a state of oxidation of Au (I); any of these can be hydrated. The rate equation is /698

$$i = 3K_{II}[AuO]\,[H^+]\,\exp\left[-\frac{\alpha EF}{RT}\right]. \quad (1)$$

where α is the coefficient of transfer and equals 0.5, while E is the potential.

Assuming that relation I is rapid and at equilibrium, the following can be written:

$$\overrightarrow{K_1}[AuOOH]\,[H^+]\exp\left[-\frac{\beta EF}{RT}\right] = \overleftarrow{K_1}[AuO]\,[H_2O]\exp\left[\frac{(1-\beta)EF}{RT}\right] \quad (2)$$

and

$$[AuO] = K\,[AuOOH]\,[H^+]\,\exp\left[-\frac{EF}{RT}\right]. \quad (3)$$

where K is a constant ($I = \overrightarrow{K}_1/\overleftarrow{K}_1[H_2O]$). The equation of the final rate is

$$i = 3K_{II}\, K\, [\mathrm{AuOOH}]\, [H^+]^2 \exp\left[-\frac{(1+\alpha)EF}{RT}\right]. \qquad (4)$$

If the oxide surface is large and well-defined as a homogeneous solid, its activity remains constant. If α from equation (4) equals 0.5, the Tafel slope will be 39 mV, in agreement with the experimental data. From the same equation it results that $(d \log i/d\ pH)_E = -2$, and the experimental value is -1.39.

The weakness of the above mechanism is the assumption that the reduction of gold (II) is a slow process. Sidgwick [55] expressed the opinion that the Au (II) compounds are in fact complex molecules which contain Au (I) and Au (III) in equal proportions. The problems which are in agreement with this opinion are not sufficiently clear as there are doubts with regard to the stability of gold in this form. Subsequently, the large field of forces which is not utilized in the adsorbed thin layer may present different stabilities depending on the states of oxidation.

Identical results are obtained if one stays on the assumption that the concentration of AuOOH is determined by the equation

$$\mathrm{AuOOH} \rightleftharpoons \mathrm{Au} + \mathrm{O_2} + \mathrm{H^+} + e^- \qquad \text{(IV)}$$

and that the limiting rate is determined by /699

$$\mathrm{AuOOH} + \mathrm{H^+} + e^- \xrightarrow{\text{slow}} \mathrm{AuO} + \mathrm{H_2O} \qquad \text{(V)}$$

Reaction (V) is followed by reactions (II) and (III) which are assumed to be rapid. This mechanism assumes that reaction (IV) is rapid and reversible at potentials around 1.2 V in 1 N perchloric acid and it requires for the reduction of oxygen on gold

a rate higher than 1000 A/cm^2, which is the observed reduction rate for the oxide at these potentials. The change of the reduction current at a constant potential is given by the equation

$$i = \alpha \exp\left(-\frac{0.20FE_a}{RT}\right), \qquad (5)$$

where E_a is the potential of oxide formation.

A comparison of equations (4) and (5) shows that the activity of AuOOH is related to the formation potential as follows

$$[\mathrm{AuOOH}] = \alpha \exp\left(-\frac{0.20FE_a}{RT}\right).$$

Qualitatively, this relation shows that the ease with which the oxide is reduced decreases with the formation potential.

It is not possible to make a correct comparison between the structures of the various gold oxides appearing as films on the anode because the above equation cannot explain the structural changes which may take place.

4. Applications of the Effect of Pretreatment

Oxidative or reductive treatment leads to oxidation, reduction or contamination of the electrode surface with adsorbed substances, and the behavior will be different in each case. In other words, the transfer function of the electrode is related to the state of the surface, which means that this function is subject to improvement by the application of appropriate treatments.

The electrochemical properties of the electrode are determined by its pretreatment and by its history, i.e., by the systems with which the electrodes had been in contact prior to its utilization.

By modifying the properties of the electrode, the pretreatment influences the reaction rates on the electrode, and this affects the reversibility of the electrochemical processes and the observed values of potential or current. These in their turn may determine the shape of the electrochemical titration curves and the precision and accuracy of the corresponding quantitative electroanalytical determinations.

The variable behavior of such electrodes depending on the applied pretreatment has made it possible to design new instrumental methods of analysis -- the bipotentiometric method at zero current -- which are based on the determination of the potential difference established during the titration of two identical electrodes with different pretreatments, immersed in solution. /700

By knowing exactly the effect of a certain pretreatment, appropriate pretreatments can be designed in order to obtain reproducible surfaces with well-defined properties, for electrodes made of noble metals and utilized in the potentiometric, amperometric, bipotentiometric or biamperometric determination of the end point of a chemical reaction [53-59].

Of particular interest are the noble metals utilized for oxygen electrodes, which facilitate interpretation of the i - E curves for superficial oxidation. Evans and Lingane [60] followed the reduction of oxygen in various media chronopotentiometrically using gold electrodes which they oxidized anodically up to the liberation of oxygen forming a surface film of oxide, followed by cathodization.

The performed investigations have led to the conclusion that in all the examined solutions, the first step in the chronopotentiogram corresponds to the reduction of oxygen to hydrogen peroxide, which is then reduced, especially in acid solutions, in the second step.

The process of aging causes a decrease in the first transition time and by the increase in over-voltage, particularly in acid solutions, the wave may disappear completely in this type of solution.

Chronopotentiometric studies have made it possible to find optimal conditions for activation of the electrode by various procedures of pretreatment. The chronopotentiometry of oxalic acid on pretreated gold electrodes was studied by Lingane [61].

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